Asymmetric Photodestruction of Bicyclo[2.2.2]oct-2-ene-5,7-dione: Absolute Configuration and ^1n-π^* Excited State Geometry

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Racemic bicyclo[2.2.2]oct-2-ene-5,7-dione (1) is partially resolved by asymmetric photodestruction with circularly polarized light. The enantiomeric purity of (1) and of its rearranged photoproduct bicyclo[4.2.0]oct-3-ene-2,7-dione (4) can be determined using a convenient formalism, essentially due to Kuhn. The absorption and c.d. of the $\beta\gamma$-unsaturated 1,4-dione (1) are reported and discussed from theory. They can be quantitatively explained in terms of an interaction of the coupled local carbonyl $n \longrightarrow \pi^*$ transitions with the ethylenic $\pi \longrightarrow \pi^*$ transition. This not only permits the assignment of the absolute configuration of (1) and, by chemical correlation, that of (4), it also opens a way to interpret the fluorescence data of (1). The emission probably originates from a locally excited carbonyl group. The circular polarization in the fluorescence indicates that the carbonyl group is no longer planar but pyramidal. The C=O out-of-plane angle is $\lesssim 40°$ in the direction of the ethylenic bond. The c.d. of (4), which is conformationally flexible and contains both an $\alpha\beta$-unsaturated and a saturated carbonyl chromophore, allows for a tentative determination of the preferred conformation.

This paper is concerned with the study of the chiroptical properties of the $\beta\gamma$-unsaturated 1,4-dione bicyclo[2.2.2]oct-2-ene-5,7-dione (1) in the $n \longrightarrow \pi^*$ absorption and $n \longleftarrow \pi^*$ fluorescence, with the main aim of acquiring information about its electronic and nuclear structure in the $^1n\pi^*$ excited state. As such it supplements and extends earlier work on $\beta\gamma$-enones.[1]

A further aspect of this paper relates to the method of enantiomeric enrichment of (1), which was available to us as a racemate only. Irradiation of racemic (1) with circularly polarized light leads to the preferential excitation and photoconversion of one of the enantiomers and eventually to partially resolved unchanged (1).[2,3] Although the method of resolution by asymmetric photodestruction is not new,[3-16] the emphasis has been on compounds available in enantiomerically pure form.[3-9] Only rarely has asymmetric photodestruction been used with the purpose of enantiomerically enriching the compound and elucidating its chiroptical properties.[15,16] We thought it of interest to study the capability and limitations of the method in a complex system like ours, where apart from (1), an enantiomerically enriched chiral photoproduct is also formed.

We here describe the photochemistry of (1), discuss some essential aspects of resolution by photodestruction, and apply the formalism obtained to our case. The optical activity of (1) in absorption and emission is reported and subjected to theoretical treatment. This leads to the assignment of the absolute configuration and to the $^1n\pi^*$ excited state geometry of (1). Additionally we report the c.d. and absorption spectrum of bicyclo[4.2.0]oct-3-ene-2,7-dione (4), a reaction product from (1).

Results and Discussion

Photochemistry of (1).—Irradiation of (1) with 313 nm light in n-pentane results in its efficient destruction (quantum efficiency of disappearance $\gtrsim 0.3$; see Experimental section), as evidenced by the decrease of the u.v. absorption at 300 nm (Figure 1). Immediately a well structured absorption develops at *ca.* 260 nm (Figure 1), belonging to phenol (2), which was identified by g.l.c. and its u.v. absorption. Apparently it is formed directly from (1) by loss of keten.† As the reaction proceeds the band at 300 nm changes in shape, pointing to a contamination of the 300 nm absorption of (1) with a less structured one, which we ascribe to (3) formed from (1) by a 1,3-acyl shift [17-20] (*cf.* Figure 2). As evidenced from g.l.c. (2) and (3) are formed in 13 and 20% yield, respectively. Direct identification of (3) failed since in a final stage of its isolation it rearranged to a product that could be identified as (4).

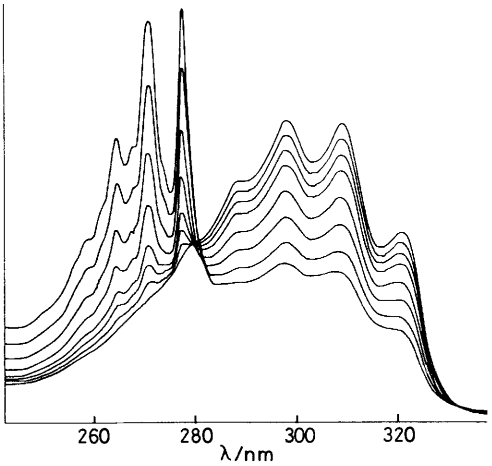

Figure 1. Change of the absorption spectrum on irradiation of (1), recorded during a preliminary small-scale experiment with unpolarized light

Although the material balance in the photoreaction is rather unsatisfactory, no other products with a yield $>3\%$ could be detected by g.l.c. When the progress of the reaction as a function of irradiation time is followed quantitatively, it appears that the concentration of (3) grows steadily until a flat maximum is reached at ρ *ca.* 0.8 [ρ denotes the proportion of conversion of (1)]. At that stage the concentration of (1) continues to decrease, while that of (2) still increases at a rate larger than the decrease of (1). Quantitatively, the increase of (2) can be explained only by a photoreaction of (3) to (2). This, and the fact that at large ρ the concentration of (3) exceeds that of (1), is taken as an indication that the photoreaction (3) $\longrightarrow$ (1), if it proceeds at all, is not very efficient.

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† Loss of keten appears to be a quite efficient photoreaction of $\beta\gamma$-unsaturated ketones, when it leads to an aromatic product.[17-19]

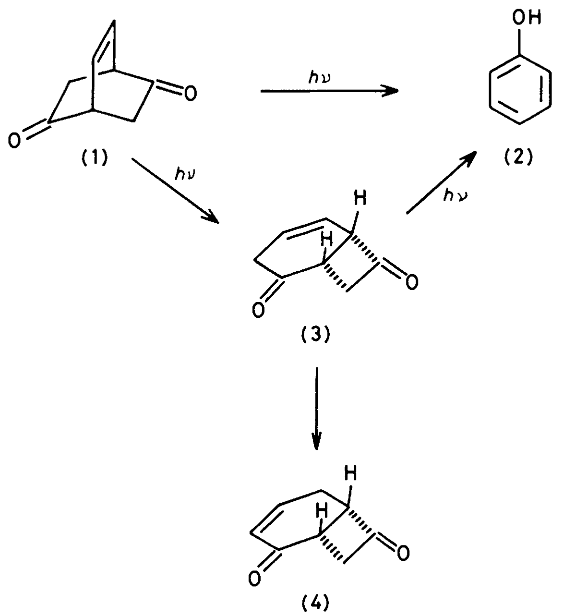

Figure 2. Reaction scheme. The depicted absolute configurations of (3) and (4) correlate with that of (1), which is the enantiomer that is preferentially destroyed

This is in line with the results obtained for the related bicyclo[2.2.2]octenones.[17–19]

Resolution of (1) *by Photodestruction.*—Irradiation of a photolabile racemic mixture with circularly polarized light results in faster photodestruction of the preferentially excited enantiomer. The resulting enantiomeric enrichment of the remaining starting material depends on the value of the dissymmetry factor at the wavelength of excitation: $g(\lambda) = \Delta\varepsilon(\lambda)/\varepsilon(\lambda)$, where $\Delta\varepsilon$ is the c.d. of the enantiomerically pure compound and ε the molar absorption coefficient. For the case that photoreaction leads to achiral products only, the development of the optical purity in the sample during the irradiation has been given by Kuhn.[3] He showed that the observed optical rotation α, as a function of ρ, is given by equation (1). In (1) α_0 is the optical rotation of the sample at ρ 0 if it were enantiomerically pure. An analogous equation holds when the optical activity is monitored as c.d., instead of rotation. Thus we have equation (2), writing c.d. as $g \,.\, \varepsilon \,.\, c_0$ (c_0 is the concentration at ρ 0).

$$\alpha(\rho) = \alpha_0 \,.\, (1 - \rho) \,.\, \tanh\left(\frac{g}{2} \,.\, \ln \frac{1}{1-\rho}\right) \simeq \alpha_0 \,.\, \frac{g}{2} \,.\, (1 - \rho) \,.\, \ln \frac{1}{1-\rho} \qquad (1)$$

$$\text{c.d.}(\rho) = g \,.\, \varepsilon \,.\, c_0 \,.\, (1 - \rho) \,.\, \tanh\left(\frac{g}{2} \,.\, \ln \frac{1}{1-\rho}\right) \simeq \frac{g^2}{2} \,.\, \varepsilon \,.\, c_0 \,.\, (1 - \rho) \,.\, \ln \frac{1}{1-\rho} \qquad (2)$$

The c.d. observed as a function of ρ at the wavelength of excitation reaches a maximum for $\rho = 1 - 1/e \simeq 0.63$; for larger ρ it again decreases as has been found by Mitchell [10] and recently by Blume *et al.*[15] Appreciating that the observed c.d. can be written as $p \,.\, g \,.\, \varepsilon \,.\, c$ one finds that the enantiomeric purity p of the remaining starting material evolves according to equation (3).

$$p = \tanh\left(\frac{g}{2} \,.\, \ln \frac{1}{1-\rho}\right) \simeq \frac{g}{2} \,.\, \ln \frac{1}{1-\rho} \qquad (3)$$

For practical purposes the simplified right hand sides of equations (1)—(3) apply to a very good approximation. For $g \leqslant 0.1$, for instance, the relative error in p due to the substitution of the hyperbolic tangent by its argument is smaller than 1% as long as $\rho < 0.8$. For still larger values of ρ the approximation is no longer warranted. Only from the exact relation (3) one may recognize that p continuously grows, approaching unity for $\rho \longrightarrow 1$ (*i.e.* vanishing chemical yield).[3,7]

To conclude we mention two practical points. So far we have assumed single-frequency irradiation. When broad-band excitation is used, $\Delta\varepsilon$ and ε, and thus g, refer to average values over the excitation band. Furthermore, the degree of circular polarization M of the excitation light will usually be <1. This has the effect that photoselection is not governed by g, but by the quantity $M.g$. In the formulae the effect is allowed for by inserting the factor M in the right hand sides of equations (1)—(3). With these understandings equations (2) and (3) allow the direct determination of p and g at any stage of the reaction, once the c.d. and ρ are known. That the formalism, given as early as 1930 by Kuhn,[3] forms a direct basis for a complete description of the evolution of optical purity in an asymmetric photodestruction experiment has not always been recognized.[15,16]

The system we have studied is more complex than that described above since, besides asymmetric photodestruction of (1), there is also asymmetric synthesis of the isomeric βγ-unsaturated diketone (3), which absorbs and shows c.d. at the excitation wavelength. It is obvious that, by itself, the presence of such a photoproduct cannot affect the evolution of p(1) as a function of ρ. (At most the photodestruction is slowed down due to capture of photons by the photoproduct.) Difficulties arise, however, if (3) is photochemically reconverted into (1). This would imply that part of the enantiomeric excess of (1) has an extraneous source, determined by the dissymmetry factor and enantiomeric purity of (3). If the formation of (3) from (1) is irreversible, the formalism given above still adequately describes the evolution of $p(\rho)$, with the understanding that in equation (2) c.d.(ρ) refers to the part of the c.d. that is due to (1). After isolation of (1) its c.d. ($= p \,.\, g \,.\, \varepsilon \,.\, c$) is readily available and allows for determination of p and g, using equation (3).

In an actual experiment on a preparative scale, which we stopped at ρ 0.55 ± 0.05 (from g.l.c.), we determined the achieved enantiomeric excess of (1) as 3.5 ± 0.3%. It is interesting to compare this value with the one we found with an independent technique that makes use of the circular polarization in the luminescence: [21] $p = 3.35 \pm 0.10\%$.[22] The close correspondence between these values strengthens our earlier assumption that the photoreaction $(3) \longrightarrow (1)$ does not occur.

If the reaction $(1) \longrightarrow (3)$ proceeds with retention of configuration, which from the mechanism of the 1,3-acyl shift [19] is highly probable, and (3) does not photodecompose to a considerable extent to (2) (see Experimental section), the enantiomeric purity of the product, p(3), and starting material, p(1), are bound to be intimately related. Both result from the same source: preferential destruction of (1). Apart from the chemical yield Y of the reaction $(1) \longrightarrow (3)$ the 'absolute

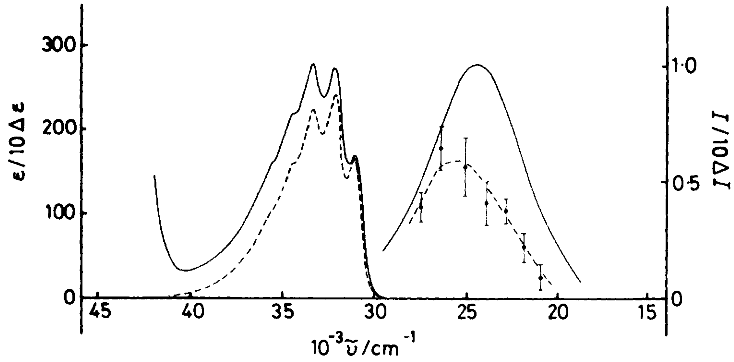

Figure 3. Spectra of (1) in n-heptane. (——) Unpolarized absorption (ε) and fluorescence (*I*), (- - -) c.d. (Δε) and circular polarization of the fluorescence (Δ*I*). The standard deviation in the Δ*I* values is given by the height of the vertical bars

Dipole and rotational strengths (units 10^{-40} c.g.s.) and dissymmetry factors

Absorption (1)	Absorption (5)	Fluorescence (1)
D_a 3 900	D_a 1 600	
R_a 72	R_a 29	
g_a 0.074	g_a 0.073	g_e 0.049

enantiomeric excesses' are equal: $\Delta c(3) = Y . \Delta c(1)$. Since at the point ρ of the reaction the total amount of (1) is $c_0(1 - \rho)$ and that of (3) $Y . c_0 . \rho$ we find that equation (4) holds.

$$p(3) = p(1) . \frac{1 - \rho}{\rho} \qquad (4)$$

Making the reasonable assumption that the rearrangement (3) ⟶ (4) also does not affect the absolute configuration [$p(4) = p(3)$] we find from equation (4) the enantiomeric purity of (4): $p(4)$ 2.8 ± 0.6%.

Electronic Spectra of (1) *and* (4).—The observed spectra of (1) are depicted in Figure 3. The position and shape of the absorption in the 300 nm region are those of a carbonyl $n \longrightarrow \pi^*$ transition; the large absorption coefficient is typical for βγ-enones.[1a,19] The c.d., observed on a sample with *p* 3.35% and corrected to 100% enantiomeric purity, is huge. From the spectra we find, using relations (5) and (6),[23]

$$D_a = 92 \times 10^{-40} \int \frac{\varepsilon}{\bar{\nu}} d\bar{\nu} \qquad (5)$$

$$R_a = 23 \times 10^{-40} \int \frac{\Delta\varepsilon}{\bar{\nu}} d\bar{\nu} \qquad (6)$$

$$g_a = 4R_a/D_a \qquad (7)$$

the dipole and rotational strengths of absorption, D_0 and R_a (Table). Integration here is over the entire 300 nm band system, which, as is discussed later on, conceals two $n \longrightarrow \pi^*$ transitions. From equation (7) we obtain the dissymmetry factor g_a.

Upon excitation (1) yields with low quantum efficiency ($\varphi_F = 4 \times 10^{-4}$) a broad structureless emission band. Since its excitation spectrum parallels the $n \longrightarrow \pi^*$ absorption band the emission belongs to (1). From the spectral analogy with other βγ-enones[1b] we assign the emission to $n \longleftarrow \pi^*$ fluorescence. The circular polarization in this luminescence (c.p.l., $\Delta I = I_L - I_R$, where I_L and I_R denote the left and right circularly polarized intensities in the emission) is large. Despite the low fluorescence yield and the low enantiomeric purity of the sample it could easily be detected. Dipole and rotational strengths in emission are found[23] as for absorption [equations (8) and (9)]. In these equations *I* denotes the average

$$D_e = 4c \int \frac{I}{\bar{\nu}^4} d\bar{\nu} \qquad (8)$$

$$R_e = c \int \frac{\Delta I}{\bar{\nu}^4} d\bar{\nu} \qquad (9)$$

$$g_e = 4R_e/D_e \qquad (10)$$

fluorescence intensity $I = \frac{1}{2}(I_L + I_R)$. Since it is obtained as a relative quantity the constant *c* is not known. The dissymmetry factor g_e however is an absolute quantity.

In order to interpret these results we first discuss briefly the nature of the lowest excited $^1n\pi^*$ states in (1). In terms of its functional groups (1) is a symmetric 1,4-dione as well as a βγ-enone. Appreciating the 1,4-dione character first, the excited state wave functions are as given in equations (11) and (12)

$$\psi_A = \frac{1}{\sqrt{2}}(n\pi^*_1 + n\pi^*_2) \qquad (11)$$

$$\psi_B = \frac{1}{\sqrt{2}}(n\pi^*_1 - n\pi^*_2) \qquad (12)$$

where the labels A and B refer to the irreducible representations in the relevant point group C_2. The indices 1 and 2 label the two carbonyl groups.

Since we know of no experimental data on the magnitude of the interaction of 1,4-diones we make an estimate from theory. Using local *n* and π^* orbitals as given by Moscowitz *et al.*,[24] we represent a local $n\pi^*$ charge density by two sets of four point charges,[25] one set around the carbonyl carbon atom, the other around the oxygen atom, both transforming as electric quadrupoles. The electrostatic interaction of $n\pi^*_1$ and $n\pi^*_2$ is then calculated using Coulomb's law. In this way it is found that due to quadrupole–quadrupole interaction the degenerate pair ψ_A and ψ_B is split by *ca.* 50 cm^{-1}, ψ_B being the lowest level.

We note that the forbiddenness of the local $n \longrightarrow \pi^*$ transitions implies that also the transitions $S_0 \longrightarrow \psi_A$ and $S_0 \longrightarrow \psi_B$ are electric dipole forbidden. The latter transitions may nevertheless acquire intensity due to coupling of the carbonyl groups if *e.g.* in (12) the mixing is not only with $n\pi^*_2$ but also with higher excited states of carbonyl (2). Perhaps this indeed happens (see later) but the considerable dipole strength we observe seems primarily due to coupling with the βγ-olefin moiety in the molecule. In a study on a series of simple βγ-enones [1a] we have found that the enhanced $n \longrightarrow \pi^*$ dipole and rotational strengths overwhelmingly result from coupling with the ethylenic $\pi \longrightarrow \pi^*$ transition and we assume a similar situation here.

Since the olefinic $\pi \longrightarrow \pi^*$ transition in (1) is of B symmetry, coupling occurs only with ψ_B to yield relation (13)

$$\psi'_B = \psi_B + \frac{\langle \psi_B | V | \pi\pi^* \rangle}{\Delta E}\,\pi\pi^* \qquad (13)$$

where the matrix element represents the electrostatic interaction between the ψ_B and $\pi\pi^*$ charge densities and ΔE is the energy separation. Thus we predict only one transition to have dipole and rotational strength, the other one is forbidden. In this picture the observed dipole strength of (1) is borrowed from the olefinic $\pi \longrightarrow \pi^*$ transition. If we assume that the latter is at 50 000 cm^{-1} and has a dipole strength of 2.5×10^{-35} c.g.s.,* the coefficient of $\pi\pi^*$ in (13) is calculated to be 0.13. From this it follows that the admixture of $\pi\pi^*$ stabilizes ψ_B by an additional amount of *ca.* 350 cm^{-1}, leading to a total splitting of ψ_A and ψ'_B of *ca.* 400 cm^{-1}.

The knowledge of the experimental rotational strength of (1) offers an opportunity to check the internal consistency of the picture. From theory the rotational strength is the scalar product of the transition's electric and magnetic dipole moments. In our picture the former is a vector in the direction of the C=C bond with a magnitude $\sqrt{D_a}$. The magnetic dipole moment in the transition to ψ'_B, resulting overwhelmingly from the ψ_B part in relation (13), is a vectorial sum of the two local $n\pi^*$ magnetic moments [*cf.* equation (12)]. When the latter is given the value [26] 1.1×10^{-20} c.g.s. the total moment in $S_0 \longrightarrow \psi'_B$ amounts to 1.4×10^{-20} c.g.s. This leads to 64×10^{-40} as an absolute value of the rotational strength,† which quantitatively corresponds with experiment. The sign of R depends on the sign of the coefficient of $\pi\pi^*$ in (13). R is positive for the absolute configuration depicted in Figure 3. Apart from supporting the picture, the calculation thus also gives the absolute configuration of (1) and, by implication, that of (4).

We note that our simple three-level description also demands that D_a and R_a of (1) are twice that of the corresponding monoketone. One way to visualize this is to expand ψ'_B in relation (13) according to (12). Rearrangement of terms then shows that ψ'_B can be written as in (14) where $\lambda_1 = -\lambda_2 = \langle n\pi^*_1 | V | \pi\pi^* \rangle / \Delta E$. This result would of course have been

$$\psi'_B = \frac{1}{\sqrt{2}}\left[(n\pi^*_1 + \lambda_1\pi\pi^*) - (n\pi^*_2 + \lambda_2\pi\pi^*)\right] \qquad (14)$$

obtained directly by letting the local $n\pi^*$ states interact with $\pi\pi^*$, before mixing them.

Since R_a and D_a of the relevant monoketone, bicyclo-[2.2.2]octenone (5), are known [24] (*cf.* Table) this prediction can be confronted with experiment. Whereas, of course, the sign of R_a is the same for (1) and (5) with equal absolute configuration, it appears that R_a and D_a of (1) are not simply twice that of (5). The small but significant (*ca.* 25%) discrepancy may in part be due to additional coupling with higher, radiative carbonyl states. Partly it may be the result of a change in geometry of (5) upon introducing a second carbonyl group. If the carbon skeleton in these bicyclo-octane compounds is not fully rigid, repulsion of the static electric dipole moments in the carbonyl groups will lead to a conformation where both groups are closer to the double bond, resulting in a larger interaction with $\pi\pi^*$ and thus in an increase of R and D. Leaving this question as it is, we yet conclude that, similar to the βγ-enones we studied before,[1a] the three-level model quite adequately accounts for the spectroscopic properties of (1) in absorption. As will be shown below this opens a way to extract information on the geometry of the fluorescent state from the emission data.

Just as the values of R_a and D_a, and thus g_a, pertain to the molecular geometry of the ground state, R_e, D_e, and g_e measure that of the fluorescent state. A difference between g_e and g_a therefore indicates that a change in geometry has occurred upon excitation. This change can be specified when D and R essentially result from the ethylenic $\pi \longrightarrow \pi^*$ transition.[1b] D_e and R_e then yield the angle between the direction of the C=C bond and the magnetic transition moment in emission. As illustrated before, magnitude and direction of the latter may be calculated if the nature of the upper state (*e.g.* ψ_A, ψ'_B, or otherwise) is known.

From the calculated energy difference between the states ψ_A and ψ'_B it appears improbable that the fluorescence arises from ψ_A. On the other hand we believe the emission does not originate from ψ'_B either. The photochemistry of (1) is remarkably similar to that of related monoketones.[17-20] Similar behaviour has been observed for other aliphatic 1,4-diketones.[28] This suggests that the excited state is characterized by a hopping of the excitation energy between one carbonyl and the other. Except for very high hopping rates one therefore expects the fluorescence to be ' localized '. The anticipated geometry changes upon excitation, assisted by solvation effects, might be held responsible for this localization. For aliphatic 1,4-diketones Lissi *et al.*[28] found the relatively low hopping rate of 2×10^8 s^{-1}.

When emission occurs from a local carbonyl excited state the interpretation of the c.p.l. may proceed along the lines used before with simple βγ-enones.[1b] That is, the decrease of g_e, compared to g_a, implies that the orientation of the C=O bond changes upon excitation. This change can be described as a distortion in the carbonyl out-of-plane direction. Since we do not know D_e from experiment we assume for a start $D_e = \frac{1}{2}D_a$. Then the observed g_e value leads to an out-of-plane angle of *ca.* 40°, where the displacement is in the direction of the ethylene bond. This however is an upper limit since it is more realistic that the dipole strength increases with decreasing C=O $\cdots$ C=C distance, *i.e.* we expect $D_e > \frac{1}{2}D_a$. As with other βγ-enones this deformation results from a binding interaction of carbonyl $n\pi^*$ and ethylenic $\pi\pi^*$ states. In the case of (1) the deformation will be assisted by a decrease of the repulsion between the static electric dipole moments of the carbonyl groups.

The absorption and c.d. spectra of (4) are depicted in Figure 4. Figure 4 also shows the relevant absolute configuration as found from chemical correlation with (1) (see Figure 2). In the long-wavelength region of the spectrum two distinct transitions can be seen. The first one at 350 nm, which is assigned to the enone $n \longrightarrow \pi^*$ transition, has a negative c.d. The other around 290 nm is ascribed to the $n \longrightarrow \pi^*$ transition of the isolated carbonyl group and shows a positive c.d. Because of the low enantiomeric purity no c.d. could be detected in the strong transition around 220 nm.

Due to the flexibility of the six-membered ring system, one expects (4) to exist in two conformations. The positive sign of

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* This value corresponds to an electric dipole transition moment of *ca.* 1 Å.e. = 4.8×10^{-18} c.g.s., as found from simple MO theory.

† Value in solution. The actual calculation of R using D proceeds *via* gas-phase values, which differ from those in solution by the Lorentz factor, taken equal [27] to 4/3.

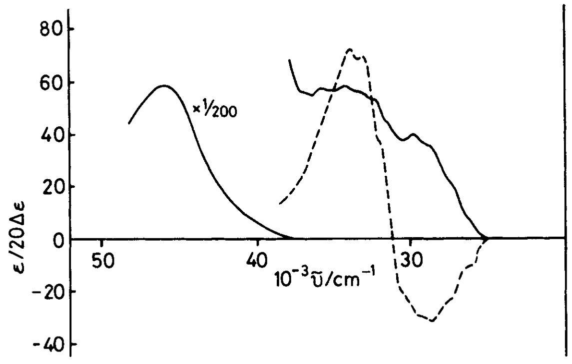

Figure 4. Spectra of (4) in n-heptane. (——) Unpolarized absorption (ε), (- - -) c.d. (Δε) corrected to 100% enantiomeric purity

the c.d. in the $n \longrightarrow \pi^*$ transition of the saturated carbonyl group agrees with that predicted from the octant rule for both conformations and thus confirms the assignment of configuration. The sense of twist in the αβ-enone chromophore is opposite in the two conformations. If the sign of the enone $n \longrightarrow \pi^*$ c.d. is ruled by the sense of twist [29] the observed negative c.d. would indicate a preference for the conformation in which the folding of the molecule is greatest.

Experimental

Racemic bicyclo[2.2.2]oct-2-ene-5,7-dione (1) (99% pure by g.l.c.) was prepared from bicyclo[2.2.2]octane-2,5-dione-7,8-dicarboxylic acid,* as in the literature.[30]

The irradiation set-up consisted of a 200-W high-pressure mercury arc (Osram), a grating monochromator (Jarrell Ash 82-410), a Glan calcite linear polarizer (Halle), and a quartz quarter-wave plate ($\frac{1}{4}\lambda$ at 280 nm). Irradiation was carried out at 313 nm with a bandwidth of 16 nm. The degree of circular polarization (M) was *ca.* 95%, determined by analysing the attenuated excitation light in the emission channel of the c.p.l. spectrometer.

For the photodestruction experiment a solution of racemic (1) (213 mg) in n-pentane (93 ml) (c_0 0.017M) was irradiated with right circularly polarized light in a specially constructed vessel with quartz windows. The solution was stirred continuously. The progress of the reaction was monitored by g.l.c. analysis and by measurement of c.d. and u.v. absorption. The degree of conversion ρ was estimated from g.l.c. The irradiation was stopped after 44 h, at ρ 0.55 ± 0.05, before (3) could photoreact to an appreciable extent. Compounds (1) and (3) were separated by column chromatography on silica. While purifying (3) it appeared to rearrange on silica.

The rearranged product was identified as bicyclo[4.2.0]oct-3-ene-2,7-dione (4) by u.v., c.d., and ^{1}H and ^{13}C n.m.r. spectroscopy, δ_H 6.9, 6.1, 3.9, 3.7, 3.3, 3.0, 2.8—2.2, and 2.0, δ_C ($CDCl_3$, SFORD multiplicity is given in parentheses) 207.16(s), 197.21(s), 148.16(d), 129.47(d), 55.64(t), 54.24(d), 33.06(d), and 22.05(t) p.p.m., $\lambda_{max.}$ (n-heptane) 335 (ε 39), 293 (58), and 217 nm (12 000), c.d. $\lambda_{max.}$ (n-heptane) 350 (Δε −1.59) and 295 nm (+3.60). The purity of (4) was *ca.* 90% by g.l.c.

G.l.c. was performed on a HP 5700 gas chromatograph (SE30 column; 130 °C). Retention times were 320 s(1), 138 s(2), 372 s(3), and 451 s(4).

Absorption spectra were measured on a Cary 219 spectrophotometer, c.d. spectra on a Jobin Yvon MIII spectrometer, n.m.r. spectra on a JEOL PS100 spectrometer. The unpolarized fluorescence and the c.p.l. spectra were recorded on a home-built instrument, described eleswhere.[31]

The fluorescence yield was determined relative to adamantanone, whose yield has been determined [32] to be 5.2×10^{-3}. The quantum efficiency of disappearance of (1) was estimated from an experiment in the c.p.l. spectrometer, where the number of photons in the excitation channel is known.

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* 5,7-Dioxobicyclo[2.2.2]octane-2,3-dicarboxylic acid.